DEVELOPMENT AND EVALUATION OF A COATING MATERIAL FOR USE IN THE COMPARATIVE CALORIMETRY METHOD OF DETERMINING SPECIFIC HEATS OF SOLIDS

By

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CHAPTER I

INTRODUCTION

Because of the accelerated rate at which modern technology is progressing, the necessity to reduce the time between the development of a new material and its application has become very important. Before the material can be used effectively, its physical and thermal properties must be known. One of the thermal properties required is the specific heat, or heat capacity, which must be determined analytically or experimentally. Since the analytical theory for specific heats in solids has not been refined sufficiently to allow analytical determination, experimental methods must be used.

The presently accepted technique for the experimental determination of specific heats of solids at constant pressure involves the use of a Bunsen Ice Calorimeter. The process consists chiefly of introducing a sample at a known temperature into a calorimeter containing a precisely measured quantity of ice. Adiabatic conditions are maintained between the calorimeter and its surroundings. The energy released from the sample as it cools to the temperature of the ice is measured by the quantity of ice melted. This process must be repeated many times to determine the heat capacity over a range of temperatures. It may be seen that this involves long periods of time.

Several people have studied methods for the rapid determination of specific heats. One method involves a furnace calorimeter in which the

rate of temperature increase of an unknown sample and the rate of temperature increase of a standard sample are measured under similar conditions. The specific heat of the unknown sample may be compared to the specific heat of the standard by comparing the respective temperature rates. Smith (1), Rea (2), Beakley (3), and Boggs (4) have found this to be a promising method.

They all suggested, however, that the accuracy of this method could be improved by coating the samples with a common material in order to obtain a surface of the same emissivity for all samples. This was necessary since the energy was transferred to the samples principally by radiation. The purpose of this investigation was to develop a suitable coating material that will withstand high temperatures and to determine its effect on the accuracy of this method.

CHAPTER II

THE METHOD OF COMPARATIVE CALORIMETRY

In comparative calorimetry, specific heat data are obtained by comparing the rate of temperature rise of a sample of unknown heat capacity with a standard of known heat capacity, each sample having a known rate of energy increase. An experimental procedure similar to that used in previous investigations was employed, but the theory was modified on the basis of a mathematical analysis.

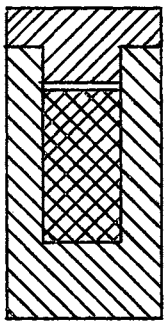


Figure 1. The Crucible

The sample was contained in a refractory crucible as shown in Figure 1 and was heated by a heater surrounding the crucible. This physical arrangement serves as the basis for the following development. These basic assumptions were made:

1) In a system of this type the only invariant is the temperature difference between two locations in the crucible.

2) After a certain finite time interval all parts of the crucible and sample experienced a temperature increase of equal magnitude in an interval of time.

3) The rate of increase of temperature was very nearly linear with time and was assumed linear for some short finite time interval.

4) The crucible behaved as an infinite cylinder.

The following equations must be satisfied for the infinite tube if the thermal diffusivity is assumed to be constant: (5)

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} = \frac{1}{\alpha}\frac{\partial T}{\partial \theta} \qquad \text{(I)}$$

where T = temperature

r = radius

α = thermal diffusivity

θ = time

$h = \frac{\partial T}{\partial \theta}$

Using assumption 2), h is a constant.

$$\alpha\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) = h \qquad \text{(II)}$$

Integrating this equation with the proper boundary conditions and solving for the heat capacity of the sample inside the crucible (the complete derivation is given in Appendix C) gives the equation

$$WC = MR - N. \qquad \text{(III)}$$

W is the mass of the sample, and C is its specific heat. M and N are independent of the heating rate at any given temperature since they are a function of geometry and parameters dependent on temperature only.

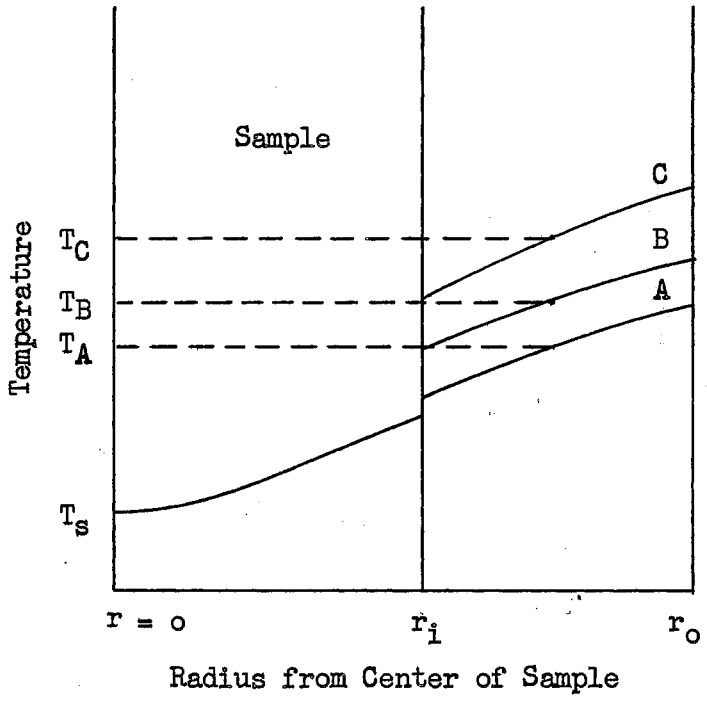


Figure 2. Temperature Distributions in the Crucible

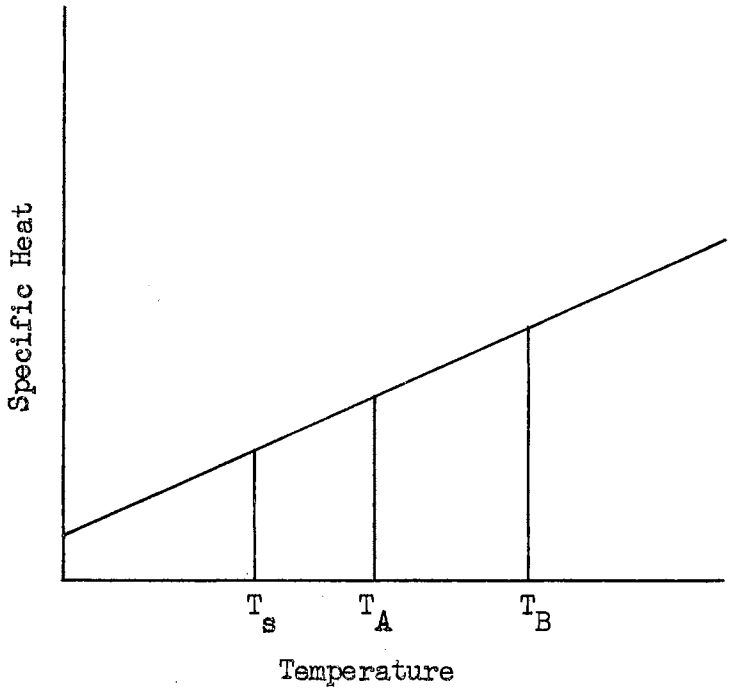


Figure 3. The Specific Heat Variation of Crucible Material

These may be experimentally determined at various temperatures by using the rates of temperature rise for two different known standards. R is the inverse of h.

Letting the subscripts c and s denote crucible and standard sample, respectively, M and N are found to take the form:

$$M = h_s(\text{Constant} \times \rho C_c + W_s C_s)$$

$$N = \text{Constant} \times \rho C_c \qquad \text{(IV)}$$

The density of the crucible remains constant. The specific heat of the crucible, which was made of fireclay brick material, increases with temperature. (6), (7). C_s may also vary, and it is evident that M and N will vary with temperature.

In determining M and N, the assumption was made that the mean crucible temperature was the same for all samples at the temperature T_s. That this was not true can be easily shown. A sample of low heat capacity would have a temperature distribution through the crucible as shown by Curve A in Figure 2. The mean temperature of the crucible would be T_A. The temperature distribution for a sample of higher heat capacity would be shown by Curve B, and T_B would be the mean temperature of the crucible. The specific heat of the crucible would be different as shown in Figure 3, and therefore M and N would tend to be different. Since this difference was a function of h also, the error should have been largely absorbed by taking standards of high and low heat capacity.

Since heat was transferred to the samples largely by radiation, a difference in the emissivities of the surfaces of the samples may magnify this error greatly. If two samples having the same heat capacities but different emissivities were compared, the temperature distributions would be shown by Curves A and C in Figure 2. The deviation in M and N caused

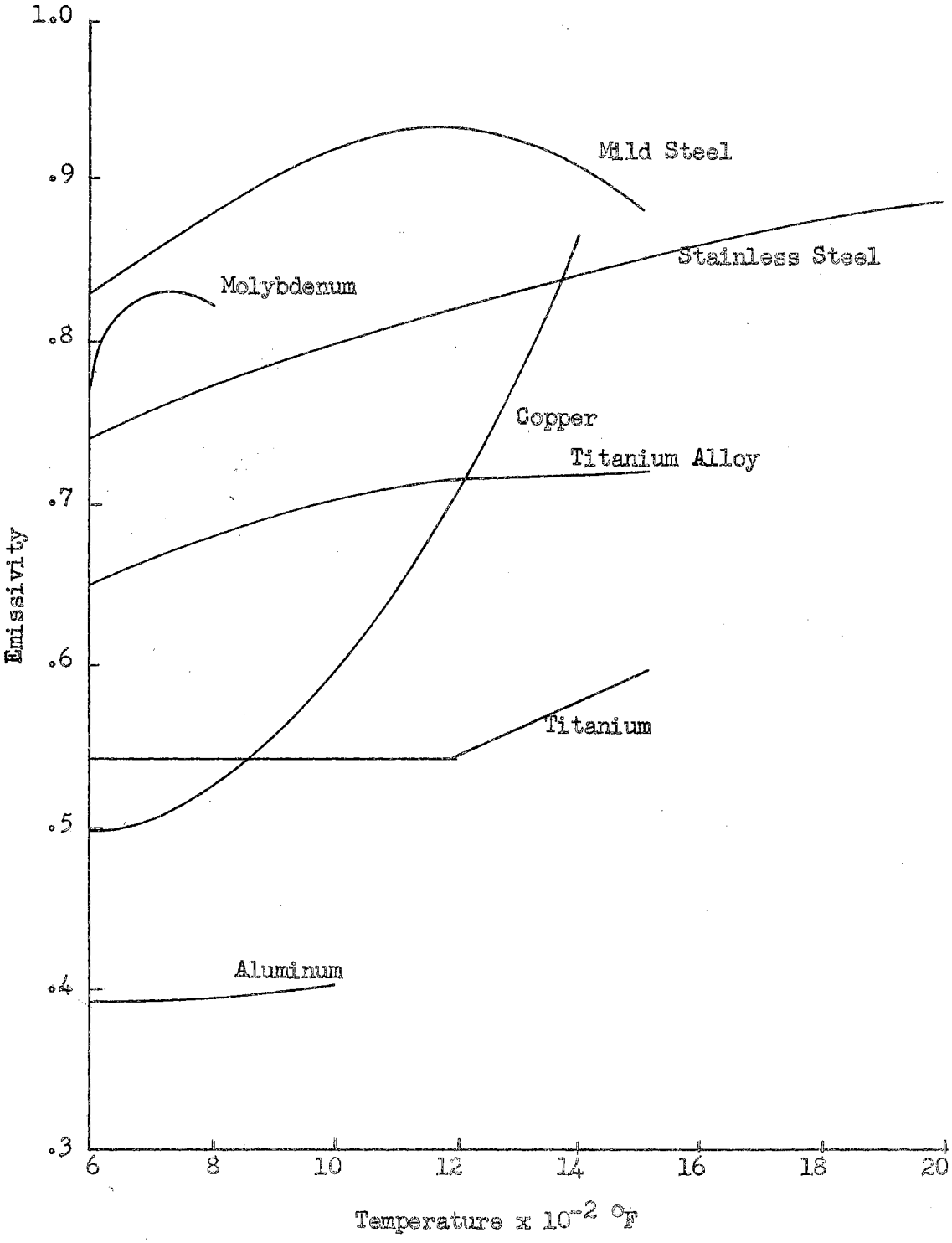


Figure 4. Emissivity of Various Oxidized Metals

by this difference would not be reconciled in the equations as before. That the emissivities of various materials differ considerably is shown in Figure 4. (8). Figure 5 also shows that the emissivity of a material varies considerably with surface condition. (9). Therefore it was

COPPER	e
Oxidized Smooth	.380
Partially Cleaned	.085
Spots and Pits on Surface	.062
Fair Polish, Some Pits	.042

Figure 5. The Effect of Various Surface Conditions on the Emissivity of Copper at Approximately 80°F

necessary to treat the surface of the samples in some manner to eliminate this probable source of error. This treatment was required to be applicable to both metals and non-metals. A common coating material, such as a paint which would have the same emissivity for all samples, seemed to be the most logical solution.

CHAPTER III

THE COATING

To be of value, the coating had to be able to withstand temperatures in the vicinity of 3000°F, preferably in a vacuum, and had to be applicable to all materials that were tested. Other requirements were that it be easily applied, inexpensive, and not require elaborate equipment for application.

Such a coating material was not found to be commercially available. One manufactured by the Norton Company, Worcester, Massachusetts, would withstand sufficient temperatures; but its method of application made it impractical.

Failure to find any such material on the commercial market led to the attempt to develop a suitable coating from materials that were available. Investigation of the high temperature properties of various materials in a vacuum quickly eliminated all but the oxides of a few metals. These were beryllium oxide, magnesium oxide, zirconium oxide, and thorium oxide. Beryllium oxide was discounted at once because of its toxic nature.

Of the remaining oxides, magnesium oxide was the most readily available and was selected for further investigation. Magnesium oxide (MgO) hydrolizes readily when it comes in contact with water. For this reason absolute alcohol, which had been used previously as a slip in slip casting,

was used as an emulsifier in an attempt to apply the coating by spraying. (10). It was found, however, that a small amount of water added to the alcohol greatly improved its spraying characteristics. With this method a coating of the desired thickness could easily be obtained. The surface was slightly rough, the larger particles of the oxide forming small lumps on the surface; but this was not expected to cause any significant error.

The magnesium oxide coating adhered to both metal and non-metal samples well for temperatures to 2000°F. No reason was seen why it could not also be used at the higher temperatures although such tests were not made because of the temperature limits of some of the equipment used. This coating seemed to fulfill all the requirements set forth earlier, and no further search was undertaken.

Investigation of the thermal radiation properties of non-metals indicated that all of the incident radiation is not absorbed at the immediate surface. Eckert (11) and Giedt (12) indicated that some non-metals require a thickness of 0.05 inch or more to be completely opaque. No reference could be found, however, that gave the thickness of magnesium oxide or any similar substance required to eliminate transmissivity. Therefore, experimental data had to be relied upon to test the effect of the coating.

CHAPTER IV

TEST APPARATUS

Test Samples, Crucible, and Crucible Base

The test samples used in this investigation were 3/4-inch diameter cylinders 1 1/2 inches long. A 1/16-inch diameter hole 3/4 inch deep was drilled in the center of the samples from one end to allow a thermocouple to be inserted into the samples. The materials for which test samples were used were vanadium, copper, synthetic sapphire (Al_2O_3), tungsten, tantalum, and molybdenum. The chemical analysis of these materials is given in Appendix B.

The samples were contained in a crucible 3 1/2 inches long and 1 1/2 inches in diameter, which was machined out of Armstrong A-28 insulating firebrick manufactured by Armstrong Cork Company, Lancaster, Pennsylvania. The cavity for the samples was made 0.80 inch in diameter to allow room for a coating and positioned so that the sample would rest in the center of the crucible. The top, which was removable, had a 1/16-inch diameter hole drilled through its center so that the thermocouple could be inserted into the sample. Holes 1/16 inch in diameter were also drilled so that the differential thermocouple could be installed as shown in Figure 6.

The crucible base consisted of a small cup 1/4 inch deep with 1/4 inch thick walls and bottom also made of the A-28 firebrick.

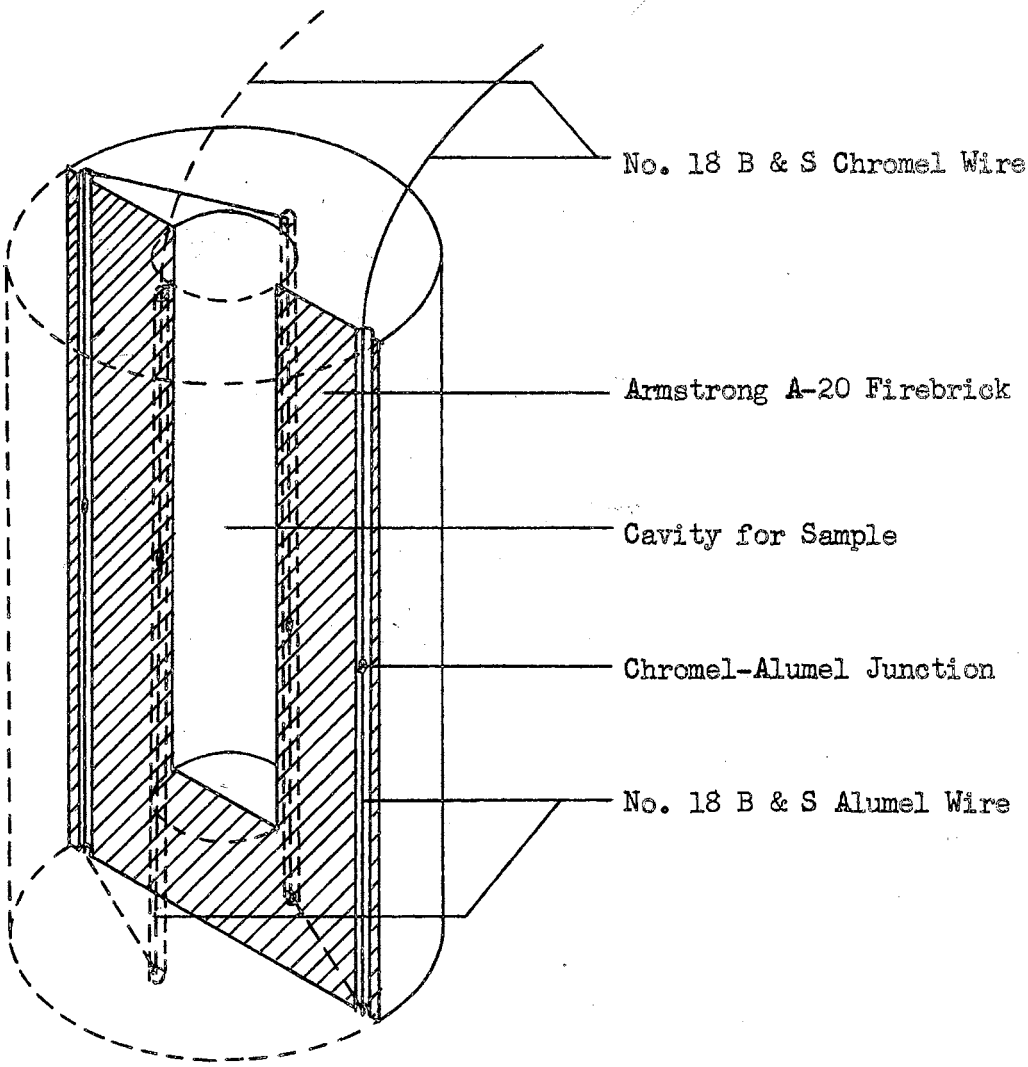


Figure 6. Schematic of the Crucible with Differential Thermocouple

Three legs made from 1/8-inch double-hole high-temperature refractory insulators were cut the proper length so that the crucible would stand in the center of the furnace and were cemented to the bottom of the cup with Sauerisen No. 63 cement. During operation, this base was placed on the bottom of the furnace and the crucible placed in the base.

The Heater

A commercial heater suitable for the purposes of this investigation was not available; therefore one was constructed. An open-filament design was used, one similar to that described by Schlapbach (13). Eighteen coils of 0.037-inch diameter molybdenum wire with an inside coil diameter of 3/16 inch, wound 12 turns to the inch, 5 inches long, were suspended vertically forming a cylindrical enclosure. Insulating rings of Johns-Manville JM-3000 insulating firebrick were used to hold the element in place and to form an electrical insulator between the element and the rest of the furnace. Short pieces of copper tubing were clamped to the ends of the filament wire, which extended out of the heated zone of the furnace, to serve as electrical contacts. Small amounts of Sauerisen No. 63 heater cement were used to attach the filaments to the insulating rings. The heated zone was a cylinder approximately 3 inches in diameter and 5 1/4 inches long.

The Enclosure

The enclosure served a dual purpose. It supported the heater element and provided sufficient heat insulation to obtain the desired temperatures with a moderate power supply. Only materials available from previous work on the project of which this investigation is a part were used.

Supporting the heater element was a cylinder of three layers of molybdenum radiation shielding, approximately 6 inches long and 4 inches in outside diameter. A calculation in the temperature region of 3000°F indicated that a fraction of an inch of insulating firebrick was equivalent to several layers of molybdenum radiation shielding in insulating property. Therefore, the molybdenum shield was surrounded by a cylinder of Armstrong A-28 insulating firebrick. The inside and outside diameters were 4 inches and 5 1/2 inches respectively, and the cylinder was approximately 7 1/2 inches long.

The radiation shield and firebrick cylinder were supported by a base made of the A-28 firebrick, which also served as a thermal insulator. A circular cover of the same material was placed on top of the firebrick cylinder. The A-28 firebrick could withstand temperatures only up to 2800°F, and additional insulation was required to lower the design temperature to 2800°F at the surface of the A-28 firebrick. The molybdenum radiation shielding was sufficient for the inside of the cylinder. However, the top and the bottom had to be protected also. This protection was accomplished by attaching circular plates of Johns-Manville JM-3000 insulating firebrick to the inside of the top cover and on the inside portion of the base. A schematic of the high temperature furnace is given in Figure 7.

To keep the surroundings at a safe temperature, the complete furnace was enclosed in a water-cooled copper shell. The shell was approximately 6 inches in diameter and 9 inches long. Radiation shields of three layers of stainless steel enclosed the top and the bottom.

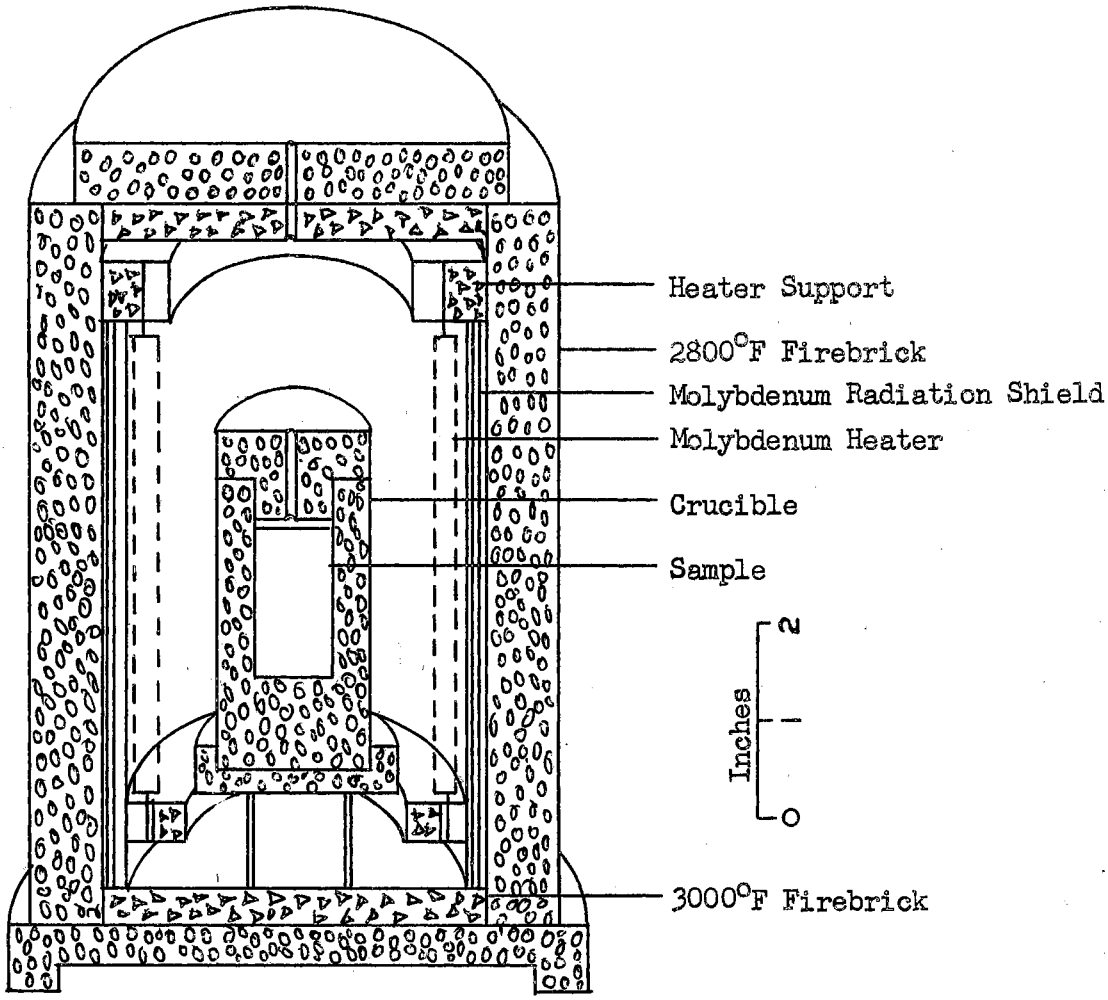


Figure 7. Schematic of the Furnace

The Vacuum System

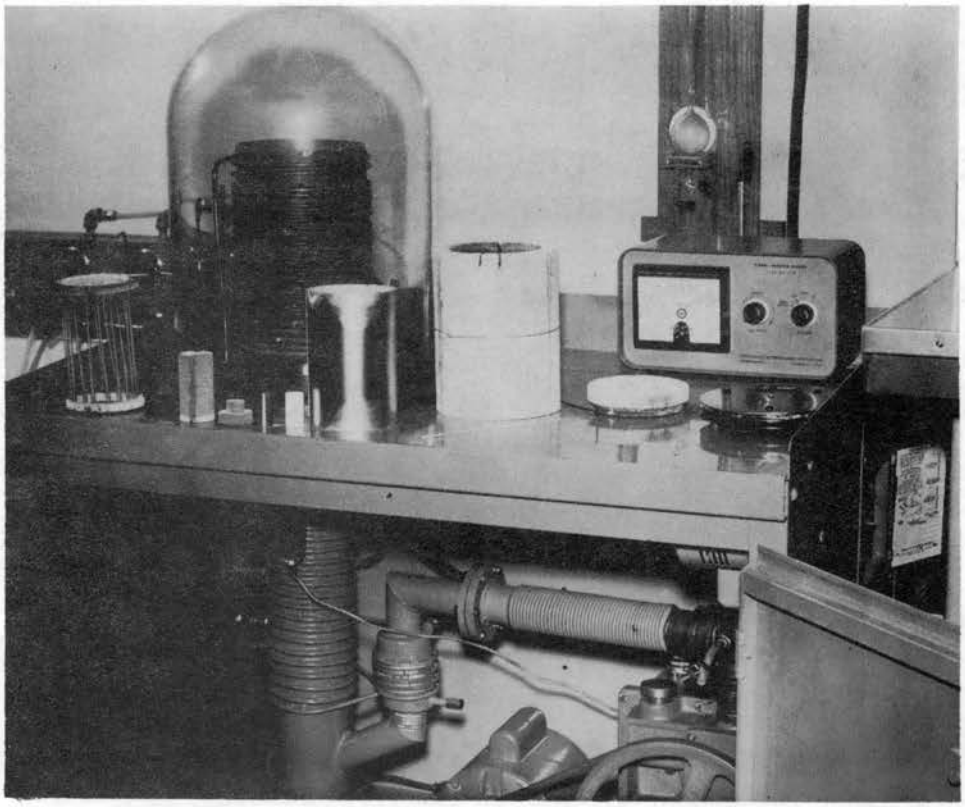
To prevent corrosive reaction at high temperatures, most materials require either an inert atmosphere, an oxidizing atmosphere, a reducing atmosphere, or a vacuum, depending on the material in question. A vacuum was selected as it was suitable for all the materials used in this investigation.

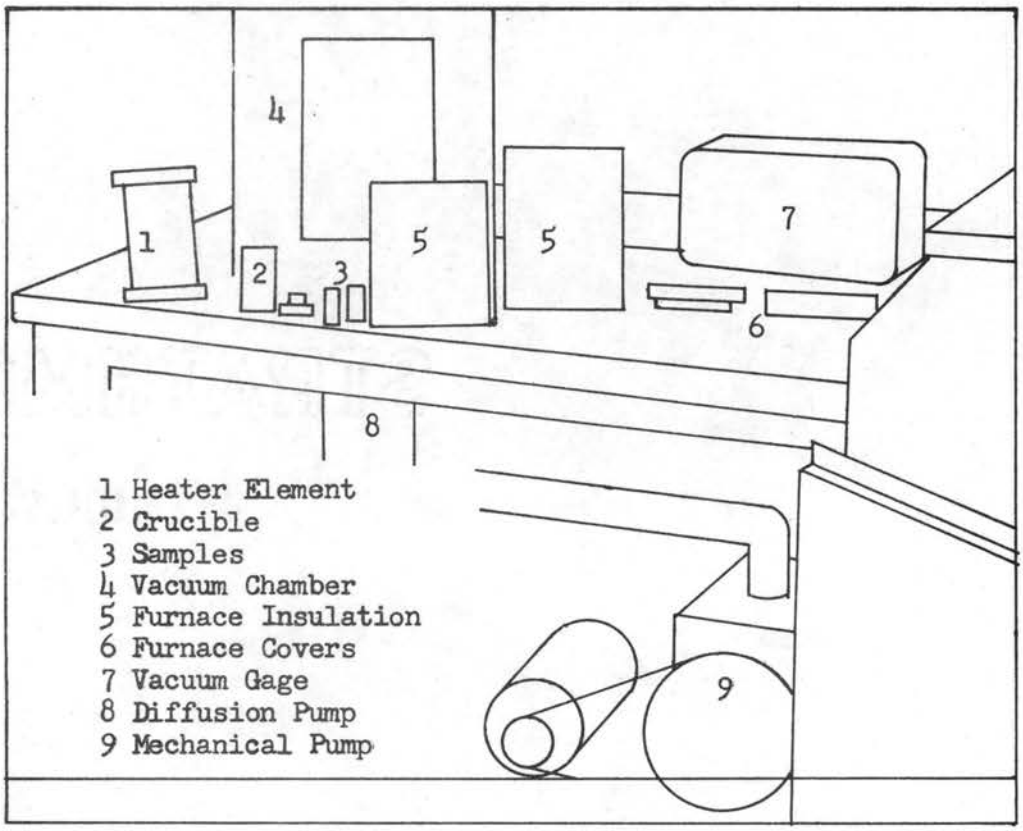
The vacuum enclosure consisted of a steel base plate on which was mounted the furnace. A glass bell jar surrounded the furnace and completed the enclosure. All cooling-water and electrical connections leading to the furnace were hermetically sealed in the base plate. To obtain sufficient vacuum, a Consolidated Electrodynamics Corporation water-cooled type MC-275 oil diffusion pump was used in series with a Welch Duo-Seal mechanical vacuum pump, Model No. 1403-B. The pressure was measured with a Pirani-type GP-110 vacuum gage. Plate I shows the vacuum system, enclosure, and the components of the furnace.

Other Instruments

All temperature measurements were made with thermocouples. The temperature gradient across the crucible wall was measured by means of a differential couple consisting of four junctions of chromel-alumel wire. They were arranged as shown previously in Figure 6. A resistance box and a galvanometer were connected in series to complete the differential circuit. By maintaining the resistance and the galvanometer reading constant, a constant potential difference in the differential couple was maintained. The resistance was necessary to adjust the galvanometer scale deflection to the proper temperature differential in the crucible.

PLATE I. THE VACUUM SYSTEM, ENCLOSURE AND FURNACE



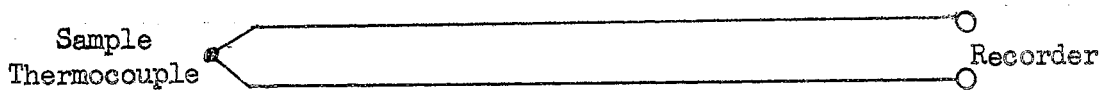


A Cenco standard resistance box and a galvanometer manufactured by the Leeds and Northrop Company, Philadelphia, Pennsylvania, having a sensitivity of 0.45 microvolt/millimeter, were used in this investigation.

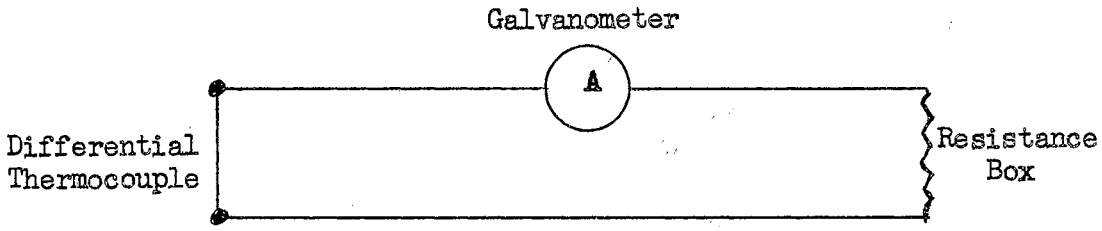
The sample temperature was measured by a platinum/platinum-10% rhodium thermocouple. This temperature was recorded on a Daystrom-Weston Model 6705 recorder, manufactured by the Weston Electrical Instrument Corporation, Newark, New Jersey. The electrical circuits for the differential and sample thermocouples are shown in Figure 8.

The electrical power for the heater was supplied by a 115-volt a-c source. Since the power required to maintain the proper heating rate varied with samples of different heat capacities and with temperature, it was necessary to control the voltage supplied to the heater. This was accomplished by using a General Radio Corporation 20-ampere Variac, series V-20. To utilize the full range of the variac scale in working with temperatures up to 1500°F, a transformer of German make having a voltage ratio of 380:220 was used to further step down the voltage.

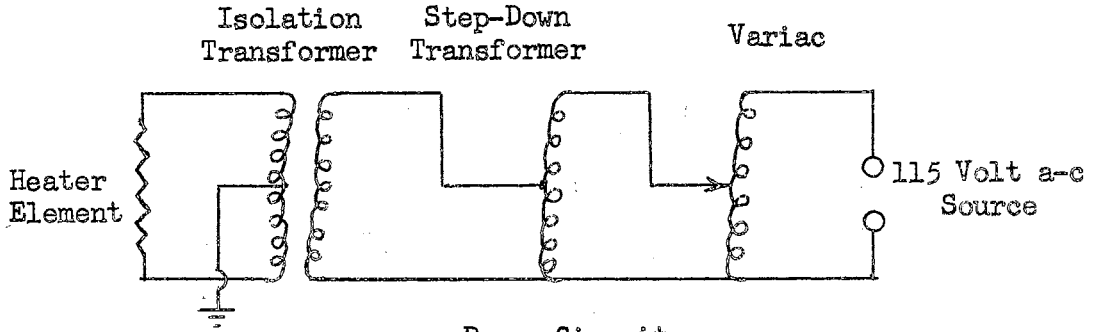
In order to minimize the potential difference between the heater element and the rest of the system, which was grounded, a specially built isolation transformer having a 1:1 ratio and center taps, manufactured by Southwest Electric Company, Oklahoma City, Oklahoma, was used with the center terminal on the output winding grounded. This gave zero potential between ground and the resistance center of the heater element. An ammeter having a 5-ampere capacity was installed in the circuit between the variac and the step-down transformer for the operator to be able to observe changes made in the power supply. This was only an aid in controlling the power input. A diagram in Figure 8 shows the electrical power circuit. The arrangement of the instruments is also shown in Plate II.



Sample Thermocouple Circuit



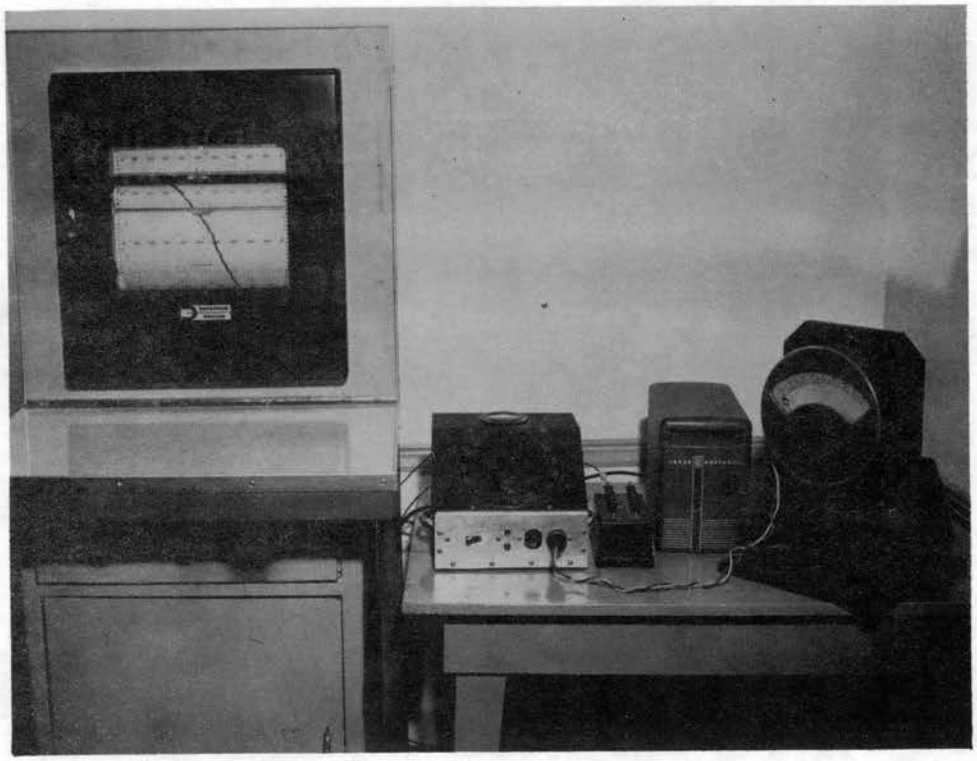
Differential Thermocouple Circuit

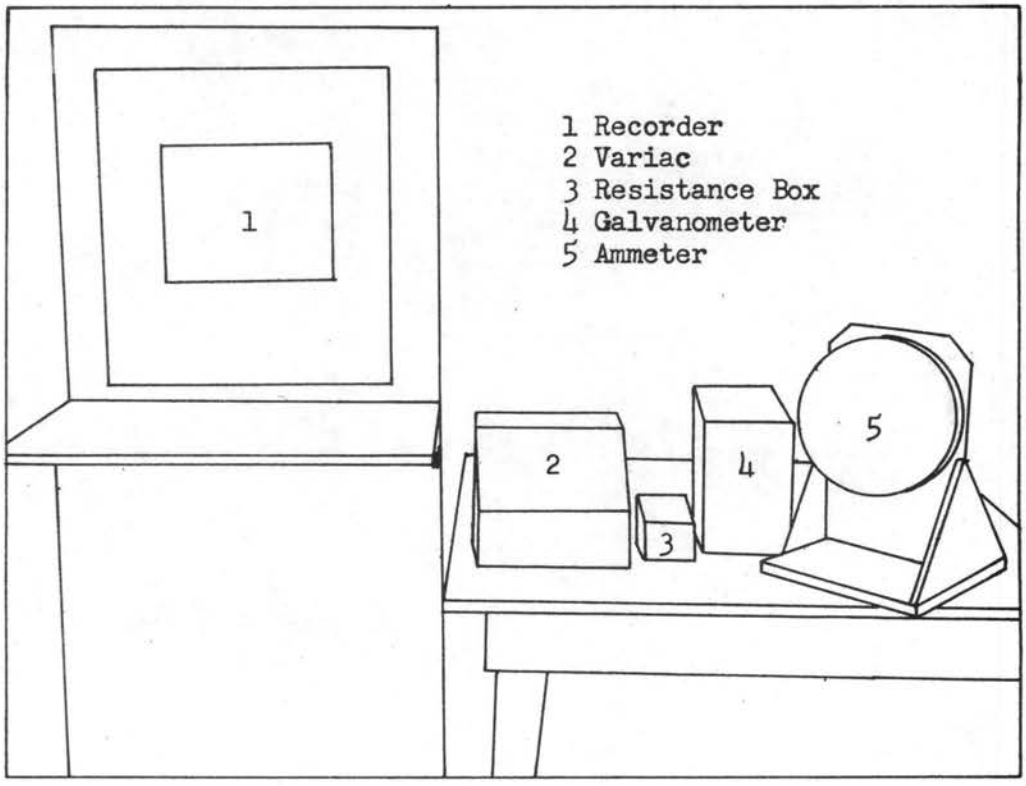


Power Circuit

Figure 8. Sample Thermocouple, Differential Thermocouple, and Power Circuits

PIATE II. OTHER INSTRUMENTS





CHAPTER V

EXPERIMENTAL PROCEDURE AND RESULTS

To be able to compare the specific heats, it was necessary to have the time-temperature relations for all samples with the same temperature difference across the crucible wall. This was the object of the experimental work.

The experimental procedure was to place the sample in the crucible and replace the furnace covers. A thermocouple was inserted into the sample from the top. A glass bell jar was placed over the furnace, and the vacuum pumps were started. To protect the operator in case of failure, a steel can was placed over the bell jar. When the system was under sufficient vacuum, the voltage was increased to the heater until the proper temperature gradient in the crucible was established. The gradient was then maintained as the temperature increased. Between 1000°F and 1500°F the sample temperature was recorded.

The furnace was then slowly cooled by gradually decreasing the voltage to the heater. Throughout the tests the flow of cooling water to the furnace was kept constant at about 160 milliliters per 15 seconds. When the tests using uncoated samples were completed, the samples were sprayed with the magnesium oxide coating; and the tests were repeated.

Some trouble was encountered with the test equipment. Originally the same equipment that Schlapbach (13) designed and built was used

except for the crucible and the electrical power arrangement. However, after a few tests the heater element failed; as a result, the furnace was redesigned. The new furnace was designed to operate at temperatures to 3000°F in order that it might be used in later investigations in the method of comparative calorimetry, although such temperatures were not necessary in this investigation. The temperature range in which tests were conducted was 1000°F to 1500°F.

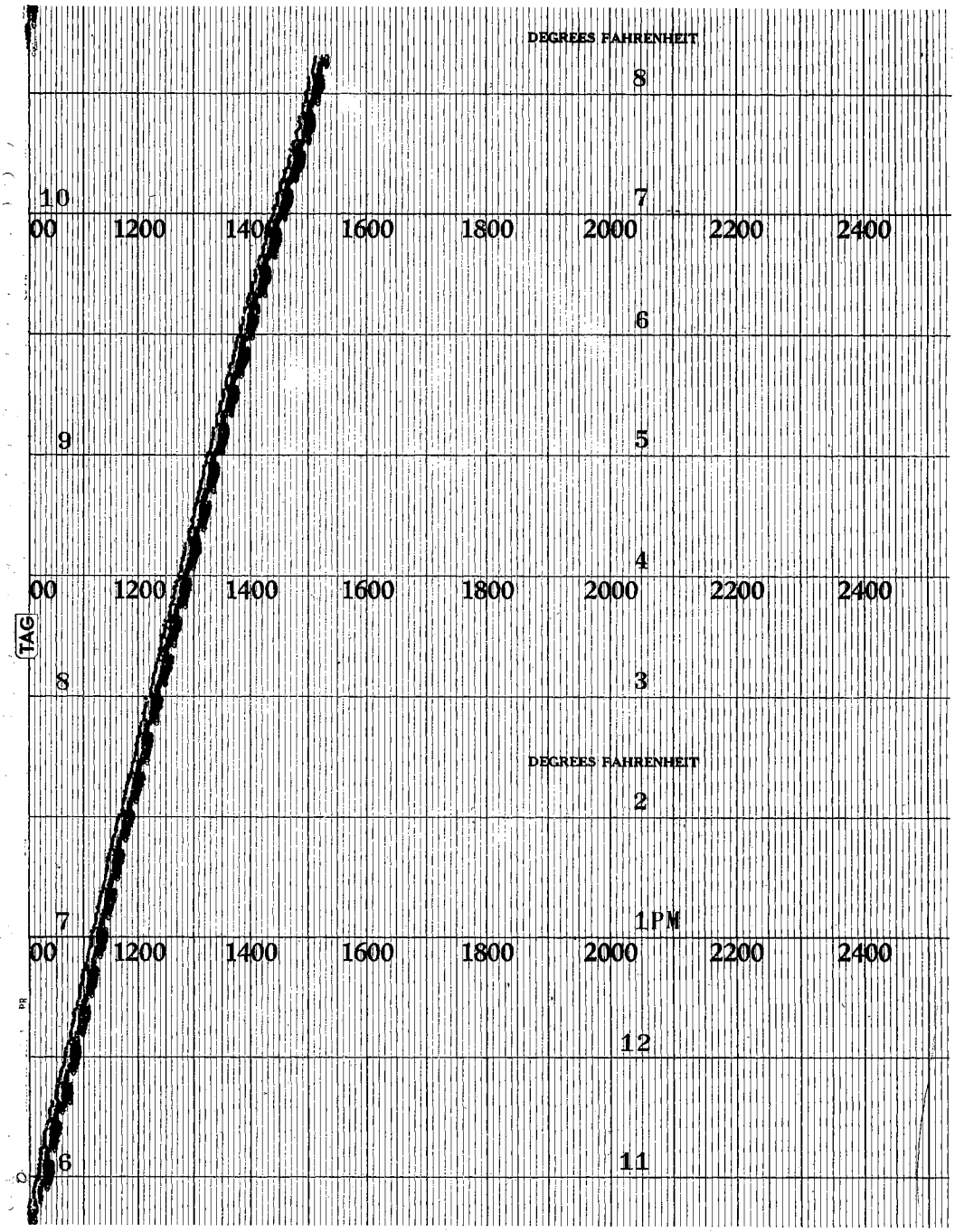
The temperature difference across the crucible wall was measured by a differential thermocouple. Since there is no direct way to keep the temperature difference constant, the potential produced by the thermocouple was kept constant. This closely approximated a constant temperature difference in this temperature range for the thermocouples used. The gradient should still be the same for all samples at a given temperature and should cause no appreciable error. The sample temperature was recorded every three seconds by the recorder which had a chart speed of 16 inches per hour. This gave the time-temperature relation for each sample. Plate III shows the original data obtained for the uncoated tantalum sample.

When the tests had been completed for all samples, the data were processed by an IBM-650 Computer (Oklahoma State University Computer Facility) using a least-squares fit to obtain the equations of the time-temperature curves secured from the experimental tests. These equations were of the form

$$\theta = A_0 + A_1 T + A_2 T^2 \qquad (V)$$

In order to stay within the range of the computer and for programming convenience, $10^{-3}T$ was used instead of T, and time intervals were taken as 1/16 hour. This change did not alter the method of calculation

PLATE III. ORIGINAL DATA FOR UNCOATED TANTALUM



since only the relative values are significant.

R is then simply $\frac{d\theta}{dT}$ or

$$\frac{d\theta}{dT} = R = A_1 + 2A_2T \qquad \text{(VI)}$$

It was found that higher order curves gave a wide variation in slope at the ends of the curves. The recorder seemed to have a slight irregularity between 1000°F and 1100°F, which may have caused this variation. Because the curves were nearly straight lines, it was decided that the quadratic equation would give the best fit; and the others were discarded. Possibly if more points over a wider temperature range were used, the higher order equations would be necessary to give a good fit over the entire curve. Table I gives the constants of the equations as determined by the computer.

The values of R were computed as shown in Table II for each sample at 100°F intervals between 1000°F and 1500°F. This was necessary since the heating rates increased slightly as the temperatures increased. The calculated values of R for the samples are given in Table III. When these calculations were completed, the constants M and N of the equation

$$WC = MR - N \qquad \text{(III)}$$

were computed by the method shown in Table IV, using synthetic sapphire and tungsten as standards. These values were also computed at 100°F intervals. For convenience the weights of the coated samples were used in calculation of both the coated and uncoated samples. The error introduced by this approximation was less than 0.5%. M and N were calculated separately for coated and uncoated sample tests. The specific heat values of synthetic sapphire given by Ginnings and Furukawa (14) were used. The probable error was believed to be less than 0.2%. The specific heat

values of tungsten were taken from Kelley's (15) values and were believed to be within 3% probable error. These two standards were used because the synthetic sapphire had a high total heat capacity and the tungsten had a low heat capacity. The specific heats of both are well known. Using the known specific heat values of other samples as standards did not give quite as good results as tungsten and sapphire.

The equation derived from the experimental values of uncoated standards was used, and the specific heats of the uncoated samples were calculated as shown in Table V. Specific heats using the coated sample data were also calculated in the same manner and plotted in graphs to show the effect of the coating. Figures 9, 10, 11, and 12 show the specific heat values determined with uncoated and coated samples, and present accepted specific heat values for tantalum, molybdenum, vanadium, and copper, respectively. The presently accepted values of specific heats of tantalum, vanadium, molybdenum, and copper were given by Kelley (15). The specific heats of molybdenum were also given by Battelle (16), Curve B, Figure 10.

Table III shows that R was consistently smaller for the coated samples than for the uncoated ones. Some samples showed a much larger decrease than others, however. Copper showed the largest decrease. Since it also had the lowest emissivity of the samples, the emissivity did seem to influence the heating rates.

The specific heat values of tantalum as measured by both coated and uncoated samples were lower than the accepted values. The maximum error for the uncoated and the coated tests was very nearly the same, about 8%. The maximum error for the uncoated test occurred at 1500°F, and for the coated test at 1000°F.

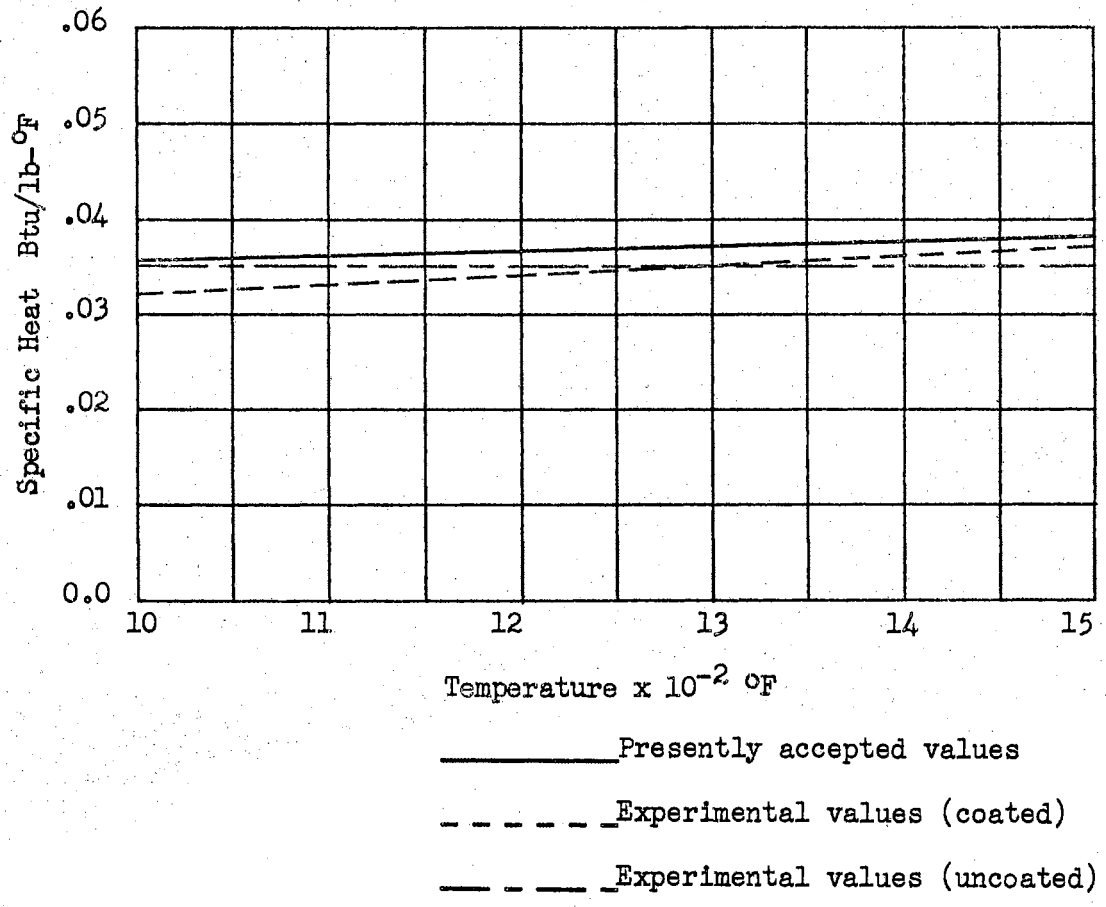


Figure 9. Specific Heats of Tantalum

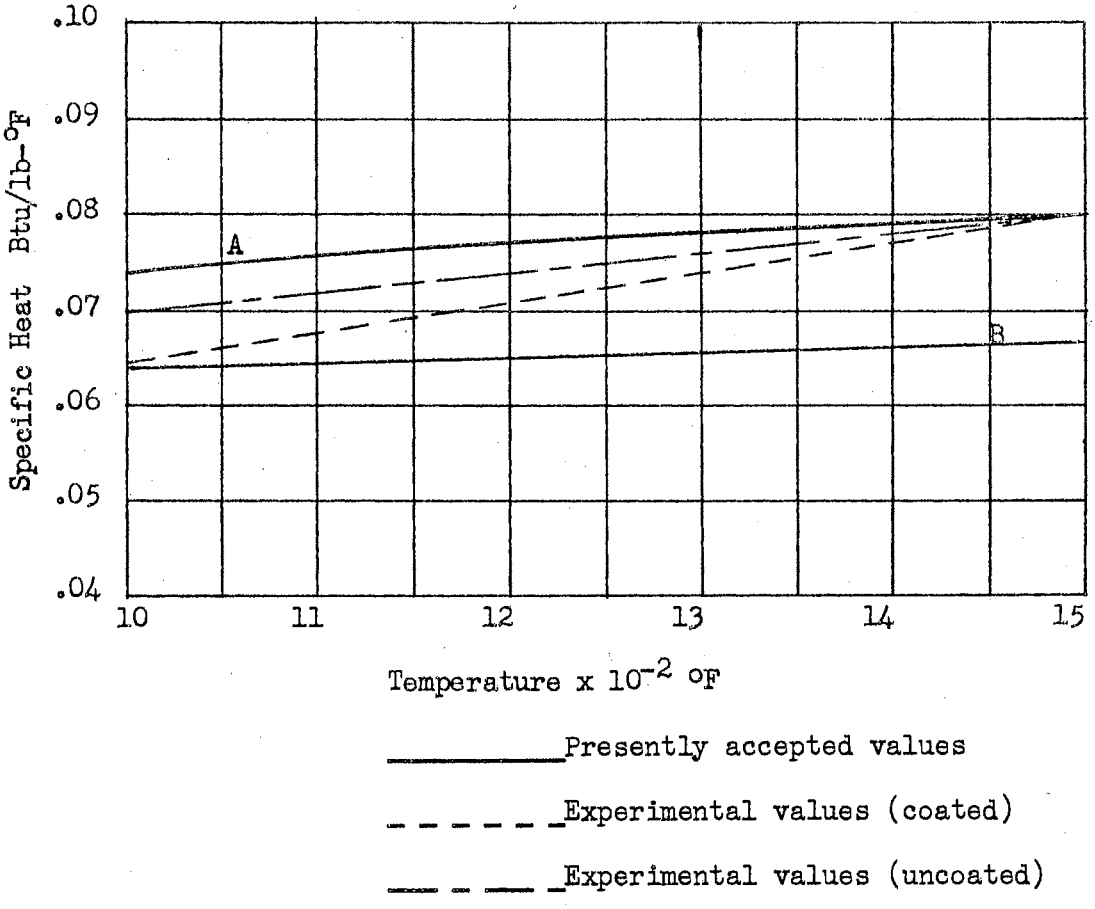


Figure 10. Specific Heats of Molybdenum

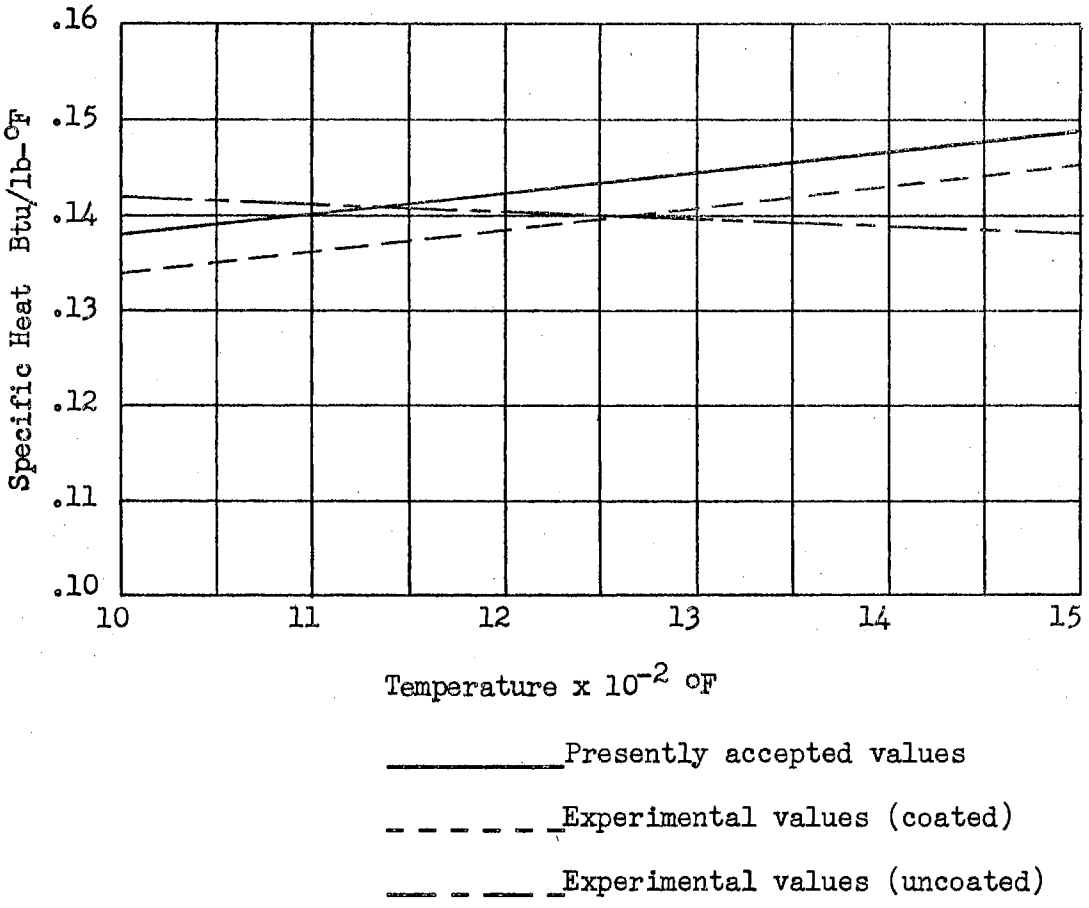


Figure 11. Specific Heats of Vanadium

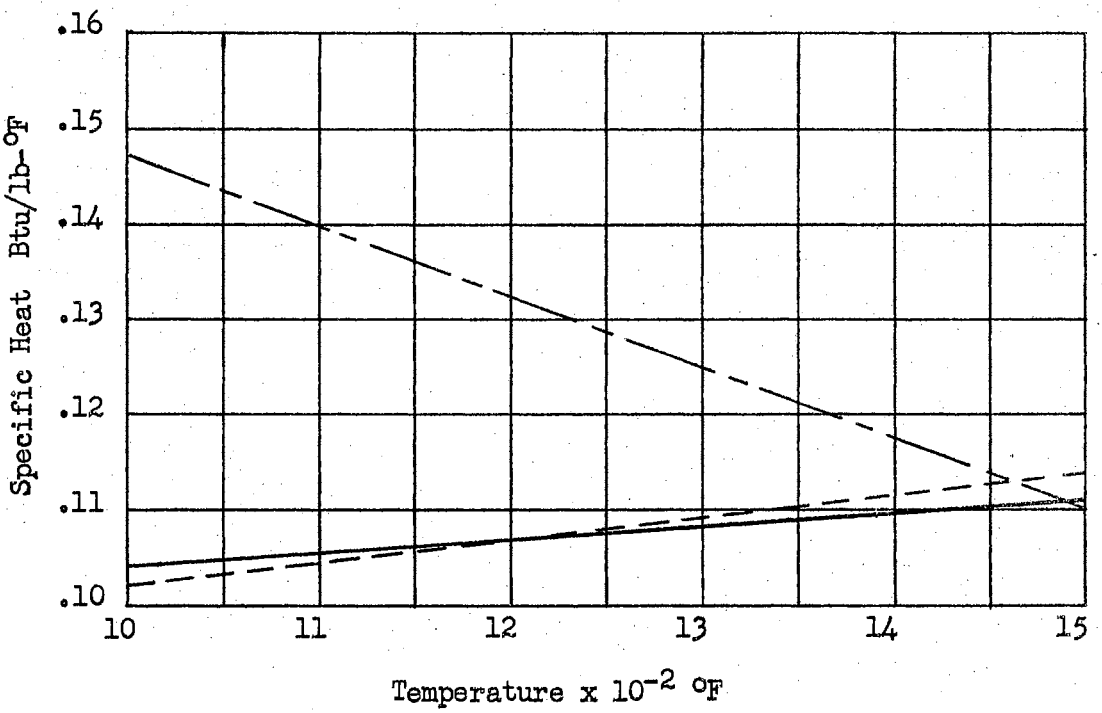


Figure 12. Specific Heats of Copper

A wide variation was discovered in the accepted specific heat values of molybdenum as given by different references. Kelley (15) presented values he believed to be within 5% probable error, Curve A, Figure 10, although they ran consistently higher than values presented by Battelle (16), Curve B. The variation was as much as 20%. Both values measured by this investigation were between those given as accepted values. However, since there is so little agreement on the specific heats, no conclusion was drawn as to the accuracy of the measured values.

The specific heats of copper determined with the uncoated sample were much higher than accepted values. The maximum error was 42% at 1000°F. Using the coated sample, much better results were obtained. The maximum error encountered by this test was about 3% at 1500°F.

Vanadium, on the other hand, showed specific heat values determined by using the uncoated sample that were too low. The maximum error here was about 7.5% at 1500°F. Again, the coated sample gave better results with a maximum error of about 2.5%.

Since emissivity varies so widely with surface condition and since no method was available to measure the emissivity of the surfaces, there was no direct method to relate emissivity of the samples and the variation in their heating rates. This must be implied from the results of the calculation of specific heats. Although the accuracy could still be improved, a definite improvement has been shown by coating the samples with a common material.

One possible reason for the errors encountered with coated samples may have been the inaccuracy of the control of the crucible temperature gradient. In the system used for this test, there was no way to improve the sensitivity of the galvanometer to variations in the temperature gradient.

Inaccuracies may possibly have arisen also from the finite length of the crucible. An error may have been introduced by the effect of heating the ends of the crucible. At low heating rates, the heater was approximately at the temperature of the crucible; and heat could have been flowing from the end of the crucible to the cooler top and bottom. For higher heating rates, the temperature of the heater was much higher than the crucible; and heat could have been flowing into the crucible from the ends. Since radiation heat transfer increases with the difference of the fourth power of the absolute temperature, this effect would increase with temperature.

Temperature differentials across the crucible wall either larger or smaller than the one used in this test might also give better results. This would have to be determined by comparing different temperature differentials and corresponding heating rates experimentally. The heating rates in this investigation ranged from 550 to 850 degrees per hour. Averaging the results of two or more runs for a given sample might give a more accurate heating rate.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are presented in the hope that they will be of benefit to others who are working in this area.

Magnesium oxide (MgO) seems to be a suitable coating material for both metal and non-metal samples. It is inexpensive and easily applied. It should be suitable for operation in a high vacuum at temperatures to at least 2900°F.

The coating of the samples definitely improves the accuracy of determination of specific heats by the method of comparative calorimetry. Although the results of this investigation contained errors of as much as 8%, it is believed this error could be reduced by improvement of instrumentation and testing procedure.

The results of this investigation seem to indicate that one of the major sources of error has been corrected, but further investigation is necessary to obtain the greatest benefit from this method. For this purpose the following recommendations are presented:

The effects of various thicknesses of the coating should be studied to insure that the influence of sample surfaces is eliminated.

The effectiveness of the coating should be investigated at higher temperatures.

A better system should be developed to maintain the temperature differential across the crucible wall more accurately.

Various heating rates should be investigated to determine an optimum.

Different crucible shapes and materials should be investigated to minimize the effects of the finite length.

The possibility of increasing the accuracy by basing the heating rates on an average of more than one run per sample should be investigated.

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APPENDIXES

APPENDIX A

CALCULATIONS

TABLE I

CONSTANTS FOR THE TEMPERATURE-TIME EQUATIONS

Sample	Run Number	a_0	a_1	a_2
Tantalum	16	-23.21	27.44	-3.513
Tantalum	19	-20.20	22.72	-1.779
Tungsten	15	-23.95	27.17	-2.619
Tungsten	18	-25.30	28.24	-3.199
Molybdenum	14	-22.83	23.40	- .364
Molybdenum	17	-22.23	22.92	- .615
Vanadium	8	-27.54	30.54	-2.515
Vanadium	12	-27.06	30.32	-2.748
Sapphire	7	-29.57	28.93	.712
Sapphire	11	-35.13	38.72	-3.633
Copper	9	-40.57	48.53	-7.397
Copper	13	-28.37	30.98	-2.169

TABLE II

COMPUTATION OF R

Sample: Al_2O_3

Run Number: 7

a_1	T	$2a_2$	$2a_2T$	R = a_1+2a_2T	Temperature
28.93	1.0	1.42	1.42	30.35	1000
	1.1		1.56	30.49	1100
	1.2		1.70	30.63	1200
	1.3		1.85	30.78	1300
	1.4		1.99	30.92	1400
	1.5		2.13	31.06	1500

TABLE III

THE VALUES OF R

Run Number	Sample	Condition	Temperature 1000	1100	1200	1300	1400	1500
16	Tantalum	Uncoated	20.31	19.71	19.00	18.30	17.60	16.90
19	Tantalum	Coated	19.16	18.80	18.45	18.09	17.74	17.38
15	Tungsten	Uncoated	21.93	21.41	20.88	20.36	19.83	19.31
18	Tungsten	Coated	21.84	21.20	20.56	19.92	19.28	18.64
14	Molybdenum	Uncoated	22.67	22.60	22.50	22.45	22.38	22.31
17	Molybdenum	Coated	21.69	21.57	21.44	21.32	21.20	21.07
8	Vanadium	Uncoated	25.41	24.90	24.38	23.87	23.36	22.84
12	Vanadium	Coated	24.82	24.27	23.72	23.17	22.62	22.07
7	Sapphire	Uncoated	30.35	30.49	30.63	30.78	30.92	31.06
11	Sapphire	Coated	31.35	30.61	29.88	29.14	28.40	27.66
9	Copper	Uncoated	33.74	32.26	30.78	29.30	27.82	26.34
13	Copper	Coated	26.64	26.21	25.77	25.34	24.90	24.47

TABLE IV

COMPUTATION OF M AND N

Standards: Al_2O_3; Weight = 43.31

Tungsten; Weight = 209.4

Sample Temperature °F	A Cp Al_2O_3	B WCp Al_2O_3	C Cp W	D WCp W	E R Al_2O_3	F R W	G B - D	H E - F	I G/H M	J I x E	K J - B N
1000	.282	12.213	.0345	7.226	31.35	21.84	4.897	9.51	.515	16.145	3.932
1100	.286	12.387	.0348	7.289	30.61	21.20	5.098	9.41	.542	16.591	4.204
1200	.288	12.473	.0350	7.330	29.88	20.56	5.143	9.32	.552	16.494	4.021
1300	.291	12.603	.0353	7.393	29.14	19.92	5.210	9.22	.565	16.464	3.861
1400	.293	12.690	.0355	7.435	28.40	19.28	5.245	9.12	.575	16.330	3.640
1500	.295	12.776	.0358	7.498	27.66	18.64	5.278	9.02	.585	16.181	3.405

TABLE V

CALCULATION OF SPECIFIC HEATS

Sample: Vanadium

Weight: 65.68

Run Number: 12

A R	B M	C A x B	D N	E C - D	F E/W Cp	Sample Temperature -°F
24.82	.515	12.782	3.932	8.850	.135	1000
24.27	.542	13.154	4.204	8.950	.136	1100
23.72	.552	13.093	4.021	9.072	.138	1200
23.17	.565	13.091	3.861	9.230	.140	1300
22.62	.575	13.007	3.640	9.367	.143	1400
22.07	.585	12.911	3.405	9.506	.145	1500

APPENDIX B

CHEMICAL ANALYSIS OF SAMPLES

TABLE VI

CHEMICAL ANALYSIS OF SAMPLES

Impurities	Tantalum	Aluminum Oxide	Molybdenum	Tungsten	Copper	Vanadium
Carbon	.005%		.003%			
Oxygen	.014%					.10%
Iron	.004%		.005%			.05%
Columbium	.050%					
Tungsten	<.020%					
Molybdenum	<.003%					
Silicon	<.020%					.05%
Titanium	<.020%					
Rhenium Oxide				.02%		
Nitrogen						<.001%
Aluminum						<.005%

APPENDIX C

SOLUTION OF EQUATION (I)

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} = \frac{1}{\alpha}\frac{\partial T}{\partial \theta} \qquad \text{(I)}$$

Since h is a constant:

$$\frac{\partial T}{\partial \theta} = h, \quad \alpha\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) = h \qquad \text{(II)}$$

The solution may be obtained as follows:

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} = \frac{h}{\alpha} \qquad \text{where } \frac{\partial T}{\partial \theta} = h = \text{constant.}$$

$$r\frac{d^2 T}{dr^2} + \frac{dT}{dr} = \frac{rh}{\alpha}$$

$$\frac{d}{dr}\left(r\frac{\partial T}{\partial r}\right) = \frac{rh}{\alpha}$$

$$r\frac{dT}{dr} = \frac{r^2 h}{2\alpha} + C_1$$

$$dT = \frac{rh}{2\alpha}dr + C_1\frac{dr}{r}$$

$$T = \frac{r^2 h}{4\alpha} + C_1 \ln r + C_2$$

but $\frac{\partial T}{\partial \theta} = h$, then $T = h\theta + f(r)$

$$T = h\theta + \frac{r^2 h}{4\alpha} + C_1 \ln r + C_2$$

Now the boundary conditions may be introduced:

Let $T = h\theta$ at $r = r_o$ (1)

$$\frac{\partial T}{\partial r} = \phi \text{ at } r = r_i \qquad (2)$$

Using boundary condition (2):

$$\frac{\partial T}{\partial r} = \frac{2rh}{4\alpha} + \frac{C_1}{r}$$

$$\phi = \frac{r_i h}{2\alpha} + \frac{C_1}{r_i}$$

$$C_1 = r_i\phi - \frac{r_i^2 h}{2\alpha}$$

Using boundary condition (1):

$$h\phi = h\phi + \frac{r_o^2 h}{4\alpha} + C_1 \ln r_o + C_2$$

$$C_2 = -\frac{r_o^2 h}{4\alpha} - C_1 \ln r_o$$

It follows that:

$$T = h\theta + \frac{r^2 h}{4\alpha} + (r_i\phi - \frac{r_i^2 h}{2\alpha}) \ln r - \frac{r_o^2 h}{4\alpha} - (r_i\phi - \frac{r_i^2 h}{2\alpha}) \ln r_o$$

$$T = h\theta + \frac{h}{4\alpha}(r^2 - r_o^2) + (r_i\phi - \frac{r_i^2 h}{2\alpha}) \ln \frac{r}{r_o}$$

Consider r_a and r_b where $r_a > r_b$:

$$T_a - T_b = \frac{h}{4\alpha}(r_a^2 - r_b^2) + (r_i\phi - \frac{r_i^2 h}{2\alpha}) \ln \frac{r_a}{r_b}$$

$$\Delta T = \frac{h}{4\alpha}(r_a^2 - r_b^2) - \frac{r_i^2 h}{2\alpha} \ln \frac{r_a}{r_b} + r_i\phi \ln \frac{r_a}{r_b}$$

From Fourier's equation for heat flow, $q = -Ak\frac{\partial T}{\partial r}$ at the inner wall.

$$\frac{\partial T}{\partial r} = -\frac{q}{Ak} = \phi$$

$$\Delta T = h(\frac{r_a^2 - r_b^2}{4\alpha} - \frac{r_i^2}{2\alpha} \ln \frac{r_a}{r_b}) - \frac{q}{Ak} r_i \ln \frac{r_a}{r_b}$$

$-q = WC\frac{dT}{d\theta} = WCh$ for the sample:

$$\Delta T = h(\frac{r_a^2 - r_b^2}{4\alpha} - \frac{r_i^2}{2\alpha} \ln \frac{r_a}{r_b}) + hWC(\frac{r_i}{Ak} \ln \frac{r_a}{r_b})$$

Let $K_1 = (\frac{r_a^2 - r_b^2}{4\alpha} - \frac{r_i^2}{2\alpha} \ln \frac{r_a}{r_b})$

and $K_2 = (\frac{r_i}{Ak} \ln \frac{r_a}{r_b})$.

Then $\Delta T = hK_1 + hWCK_2$

$$\Delta T = h(K_1 + WCK_2)$$

Now if ΔT is kept at the same constant value for a standard and an

unknown:

$$\Delta T = h_u(K_1 + W_uC_uK_2)$$

$$\Delta T = h_s(K_1 + W_sC_sK_2)$$

$$0 = h_u(K_1 + W_uC_uK_2) - h_s(K_1 + W_sC_sK_2)$$

$$h_u(K_1 + W_uC_uK_2) = h_s(K_1 + W_sC_sK_2)$$

$$K_1 + W_uC_uK_2 = \frac{h_s}{h_u}(K_1 + W_sC_sK_2)$$

$$W_uC_uK_2 = \frac{h_s}{h_u}(K_1 + W_sC_sK_2) - K_1$$

Let $R_u = \frac{1}{h_u}$.

$$W_uC_u = R_uh_s(\frac{K_1}{K_2} + W_sC_s) - \frac{K_1}{K_2}$$

Let $M = h_s(\frac{K_1}{K_2} + W_sC_s)$

and $N = \frac{K_1}{K_2}$.

M and N are independent of the heating rate at any given temperature since they are a function of geometry and temperature dependent parameters only.

$W_uC_u = MR_u - N$ and generalizing

$$WC = MR - N \qquad \text{(III)}$$

M and N may be determined experimentally at various temperatures by using the rates of temperature rise for two different known standards.

Now let $U = \frac{r_a^2 - r_b^2}{4} - \frac{r_i^2}{2} \ln \frac{r_a}{r_b}$

$$V = r_i \ln \frac{r_a}{r_b}$$

Both U and V are functions of the geometry of the crucible and will be constants for all samples and throughout the range of temperature.

$K_1 = \frac{U}{\alpha}$ and $K_2 = \frac{V}{k}$

$$M = h_s\left(\frac{K_1}{K_2} + W_s C_s\right) = h_s\left(\frac{Uk}{V\alpha} + W_s C_s\right)$$

$$N = \frac{K_1}{K_2} = \frac{Uk}{V\alpha}$$

But $\alpha = \frac{k}{\rho C_c}$

$$\frac{Uk}{V\alpha} = \frac{Uk\rho C_c}{Vk} = \frac{U}{V}\rho C_c$$

$$M = h_s\left(\frac{U}{V}\rho C_c + W_s C_s\right), \quad N = \frac{U}{V}\rho C_c \qquad \text{(IV)}$$

APPENDIX D

NOMENCLATURE

SYMBOLS

T	Temperature.
r	Radius.
α	Thermal diffusivity.
θ	Time.
h	$\frac{\partial T}{\partial \theta}$.
R	$\frac{1}{h}$.
ρ	Density.
q	Heat flowing from crucible to sample.
k	Thermal conductivity.
A	Area.
e	Emissivity.

SUBSCRIPTS

c	Crucible.
s	Standard sample.
o	Outside.
i	Inside.
u	Unknown.

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